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(54) Anti-blocking agents with improved dispersability in polyolefin films and methods for making and using the same

(57) A dispersible, porous particulate anti-block for polyolefin films is prepared by combining porous inorganic oxide, e.g., silica, with a surface active agent, e. g., a polar fatty acid ester, to form a particulate comprising both components. The particulate can be added as an anti-block agent to the polymer used to make the polyolefin film. The particulate has an average particle size in the range of about 1 to 20 microns and a carbon content in the range of about 1 to about 15% by weight of the inorganic oxide and ester. It has been unexpectedly discovered that a particulate prepared in this fashion is more readily dispersed compared to adding anti-block and conventional ester dispersants separately.

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Description

BACKGROUND OF THE INVENTION

[0001] This invention relates to particulates which are suitable as anti-blocking agents for plastic films. The invention more particularly relates to highly porous anti-blocking particulates and methods for rendering them more dispersible in polymers used to make the films.

[0002] Porous particulate inorganic oxides, e.g., silica gels, are widely used as anti-blocking agents in polymer films, especially polyolefin films. Anti-blocking agents for these films typically have average particle sizes in the range of 1 to 20 μm, and generally are incorporated into the films in concentrations ranging from 0.001 to 2.0% by weight. It is believed that these particles produce microscopic surface deformations which reduce contact between two surfaces of films lying on one another, thereby facilitating the separation of those surfaces, e.g., separating the two sides of a bag or the unwinding of film from a roll. The resistance to separation is called "blocking" and agents added to reduce the resistance impart what is called "anti-blocking".

[0003] Synthetic amorphous silica gels are particularly suitable for anti-blocking. They have a relatively large specific pore volume (porosity) and provide a larger number of particles (of a certain size) per gram than products with lower porosity (e.g., talc, chalk, naturally occurring silica such as diatomaceous earth). For these reasons, micronized porous synthetic silica gels are known to be more effective anti-blocking agents than products with low or no porosity.

[0004] Anti-blocking agents can be sold directly to polymer resin manufacturers or more typically sold to film manufacturers as masterbatches. Masterbatches are prepared by adding the anti-block agent at high loading into a base polymer. These masterbatches are then processed through an extruder to prepare masterbatch pellets. The pellets are added as concentrates to a polymer resin which is then itself processed through a film extruder to form the polyolefin film.

[0005] Relatively highly porous and-block particulates, however, can agglomerate into larger particles before and/or during mixing to make the mascerbatch or during the masterbatch extrusion process to make pellets. These large agglomerates are difficult to break up and, as a result, they can be present when the masterbatch exits the extruder. This leads to frequent blockages of screens which filter out unmolten polymer particles and undispersed additives. Blockages in turn cause lower production output.

[0006] These agglomerates also lead to inferior film product. More specifically, these agglomerates are known to cause imperfections called "nibs or fish eyes". These nibs appear as holes or blemishes in the films. Because porous inorganic oxides such as amorphous silica gel are efficient anti-blocking agents, there is a need to decrease their tendency to agglomerate and/or improve their dispersability to reduce the creation of nibs, yet do so without detrimentally affecting the agent's performance.

[0007] In the field of architectural coatings, it is known that the dispersability of flatting agents made from porous inorganic oxide particulate can be improved by coating the flatting agent with polyolefin wax. Untreated flatting agents can settle over time and the resulting sediment is then difficult to redisperse. Wax treated agents, on the other hand, are more easily redispersed after settling. The same type of treatment has been suggested for film pigments and colorants to improve their dispersability, but has met with limited success.

[0008] Dispersible silica and/or alumina particulates in the size range of 30-50 millimicrons have been described in UK 1,109,840. The particulates mentioned in this application are treated with surface active agent in amounts ranging from 10 to 600 parts per 100 parts particulate. Among the many agents mentioned, sorbitan monostearate and other particular fatty acid esters are mentioned. The preferred embodiments described however contain high amounts of organic, e.g., 50 parts surface active agent per 100 parts particulate. The reference also only mentions particulates in the range of 30-50 millimicrons and only discloses using those particles in applications typically associated with such fine sized particles, e.g., reinforcing agents for rubber and pigments for paint. There is no mention of treating particulates suitable for anti-blocking, i.e., those having particulate sizes in the range of 1 to 20 microns.

[0009] Surface active agents mentioned in UK 1,109,840, e.g., sorbitan monostearate, have also been described as dispersing agents for inorganic additives used to reduce haze in olefin films. See U.S. 4,490,502. U.S. 4,560,609 also describes sorbitan monostearate as a dissolution agent for an inorganic additive which is used to impart heat retention in polymer films. Each of these patents suggests adding those agents to the film's polymer base separately from the inorganic additive. As indicated later below, when such organics are added to films containing conventional anti-blocking agents, an unacceptable amount of nibs still occur.

[0010] Other fatty acid esters have been mentioned as anticaking agents (U.S. 4,288,460) and refractive index modifiers for films (U.S. 4,415,691). However, the references above do not describe or suggest solutions to improving dispersability of particulate porous inorganic oxides suitable for anti-blocking agents. Therefore there is a need to continue improving the dispersability of porous inorganic oxides so as to maximize the value of these highly efficient agents.

SUMMARY OF THE INVENTION

[0011] A readily dispersible porous particulate anti-block for polymer, e.g., polyolefin, films can be prepared by combining conventional porous particulate inorganic oxides with polar surface active agents such as phosphoric acid ester or fatty acid ester prior to adding the inorganic oxide to the polymer base used to prepare the film. It has been found that the mere addition of a surface active agent such as those above to a mixture of polymer and anti-block agent does not provide satisfactory results. On the other hand, Applicants have noted significant improvement in the anti-blocking agent's dispersability when a surface active agent is intimately mixed with the anti-block before it is added to the polymer base.

[0012] The dispersability is further improved if the two components of the invention are combined so that the surface active agent is coated onto the particulate porous inorganic oxide. The surface active agent is preferably added to the anti-blocking agent in amounts such that the final particulate product has a carbon content in the range of about 1 to about 15% by weight based on the total weight of the surface active agent and inorganic oxide. The final particulate also has an average particle size of conventional anti-blocking agents, e.g., about 1 to 20 microns.

DETAILED DESCRIPTION

[0013] Porous Inorganic Oxide. The porous inorganic oxide of the invention can be those particulates typically used as anti-blocking agents. Such particulates include micronized amorphous silica gel (e.g., xerogel), precipitated silica and the like. The pore volume for these particulates can range from 0.3 to 2.0 cc/g. While less porous particulates can benefit from this invention, those particulates which have a pore volume of at least 0.6 cc/g are more suitable because those agents have a higher pore volume and are more difficult to disperse than products having a smaller pore volume. The products having smaller pore volumes also are less effective at providing anti-blocking and therefore are less suitable for a number of anti-block applications. Particulates having pore volumes in the range of 0.8 to 2.0 cc/g are even more suitable. Porous particulates and the methods for their manufacture are well known.

[0014] Traditional amorphous silica gel anti-blocking agents are preferably prepared by milling and drying a base silica gel to an average particle size in the range of about 1 to 20 microns, as measured by a Mastersizer (light scattering) particle size analyzer instrument from Malvern. The surface areas of the traditional porous anti-blocking particulate are in the range of 100-650 m^2/g. Higher pore volume silicas have surface areas in the range of from about 250 to about 500 m^2/g and have average pore diameters of 7 to 50 nm. The pore volumes reported herein are measured by conventional nitrogen porosimetry and surface area is measured using the BET technique.

[0015] Suitable porous precipitated silicas include those described in "The Chemistry of Silica," Ralph K. Iler, A Wiley-Interscience Publication, John Wiley & Sons (1979), e.g., pp. 554-560, thereof. Such precipitated silicas have pore volumes in the range of 0.1 to 0.8 cc/g, surface area of 50-500m^2/g and an average particle size of 2 to 15 microns: Methods for making precipitated silica are known in the art as shown in the above-mentioned "The Chemistry of Silica".

[0016] Surface Active Agent. Suitable active agents are those which are polar and have an ester linkage. Such agents are known and described in the literature. See Kirk Othmer's Encyclopedia of Chemical Technology, 2d Edition, Vol. 19, pp. 507-593. Suitable surface active agents include phosphoric acid esters and fatty acid esters. Suitable phosphoric acid esters include, but are not limited to, 2-ethylhexyl phosphateoctyl phosphate, decyl phosphate, dodecyl phosphate, octadecyl phosphate, 9-octadecenyl phosphate, mixed alkyl phosphates, hexyl polyphosphate, 2-ethylhexyl polyphosphate, octyl polyphosphate, and decyl polyphosphate.

[0017] Suitable fatty acid esters include, but are not limited to, fatty ester acids of polyhydric alcohols such as fatty acid monoglycerides, fatty acid sorbitan esters, fatty acid polyglycerin esters, fatty acid trimethylol propane esters, fatty acid pentaerythritol esters and the like. Particularly preferred embodiments include glycerin monostearate, sorbitan monostearate and sorbitan monooleate. Other suitable agents include sorbitan monolaurate, sorbitan tristarate, and sorbitan esquioleate. Alkylene oxide adducts of the above compounds may also be used. Such adducts include polyoxyethylene monooleate, polyoxyethylene sorbitan monolaurate, polyoxyethylene monostearate, and polyoxyethylene monolaurate.

[0018] The porous inorganic oxide particulate and polar surface active agent are combined in a manner to produce a particulate having an average particle size in the range of about 1 to about 20 microns and a carbon content of about 1 to about 15% based on the weight of the inorganic oxide and surface active agent. Preferred particle sizes are in the range of 1 to 12 microns, and more preferably in the range of 1 to 7 microns. Other preferred embodiments have particles sizes in the range of 10-12 microns.

[0019] The surface active agent is added in an amount effective to disperse the antiblocking particulate in a polymer. The amount added is reflected by the carbon content in the final product. The carbon content of the invention is in the range of l to 15%, but preferably in the range of l to 10% by weight of the particulate and surface active agent. Reference to carbon content herein is used to mean the amount of carbon present in a particular sample. For example, if a coated particulate is combusted with excess oxygen at 1450° C, any hydrocarbon present is converted to carbon dioxide and

water. The water is removed and the resulting dried gas is fed through an infrared cell at a controlled rate, e.g., 4 1/min. The concentration of carbon dioxide in the stream is then measured by an analyzer, e.g., an SC-444 Analyzer from LECO. That concentration is converted into a percentage/(ppm) carbon value taking into account the sample weight, calibration and known moisture value. In most instances, the above carbon content can be obtained by adding about 5 to about 20% by weight surface active agent based on the weight of inorganic oxide.

[0020] The invention can be prepared by combining and intimately mixing surface active agent and a finished anti-blocking particulate in a mixer or fluidized dryer. In this embodiment, the particulate is first pre-milled to the average particle size desired for the final product and then the milled particulate and surface active agent are added to a mixer or dryer. The surface active agent can also be added to the inorganic oxide particulate as the particulate is being milled to its final average particle size. This procedure can be conducted in a jet mill or fluidized energy mill designed to intimately and thoroughly mix materials. Both methods are illustrated in the examples below.

[0021] Either method can be used to produce particulate consisting essentially of inorganic oxide and surface active agent, e.g., as the only two components or including minor amounts of additional component(s) which do not affect the properties of the particulate. When using either of the above-described methods, it is preferred to choose conditions which produce a coating of surface active agent on the inorganic oxide particulate. This is generally accomplished by heating the mixer or mill as the materials are blended or otherwise put in contact with one another. In certain instances, there is a need to heat the mixture of surface active agent and particulate to the surface active agent's melting point, e.g., when using a Henschel mixer. The particular mill or mixer chosen, heating temperatures, and mill or mixer residence times, however, depend on the porous inorganic oxide, desired average particle size, desired drying content and the particular surface active agent chosen. For most processes the coating temperature used is in the range of 55 to 200° C.

[0022] Another less preferred method is to combine the inorganic oxide and surface and add the mixture "as is" to an additive inlet to an extruder used to make masterbatch pellets or film. Modification and selection of the parameters for each of the above-described methods is within the knowledge of those with ordinary skill in the art. See, U.K. 1,109,840.

[0023] The invention can be incorporated into polyolefin polymer, e.g., polyethylene and polypropylene, using conventional techniques and conventional amounts. Those amounts can be in the range of 0.001 to 2.0% by weight of polymer, while in most typical applications used in amounts of 0.01 to 0.5% by weight. The invention can also be incorporated into a polymer masterbatch. In that case the invention is added to polymer at high concentrations, e.g., 80-95 wt. % polymer plus 5-20 wt. % invention. Masterbatches are prepared by combining the polymer and anti-block in equipment such as Banbury mixers, internal kneaders or screw kneaders to make pellets or powder. The pellets or powder is then fed into an extruder to make film. In case a masterbatch is used, the masterbatch is mixed with the polymer granules in such a ratio as to obtain a final anti-blocking aid concentration of 0.01 to 0.5% by weight of polymer. Extruding the film from a masterbatch is well known in the art. Suitable film preparation methods are disclosed in U. S. Patent 4,327,009 or U.S. Patent 4,415,691, the contents of which are incorporated by reference. Typical films in which the invention can be used in films having a wide variety of film thicknesses. Generally, the invention can be used with films having thickness in the range of 0.5-100 microns. The anti-blocking agents of the invention show an anti-blocking effect which is at least equal to that shown by untreated anti-blocking agents.

[0024] The following examples of the invention are illustrative and are not intended to any way limit the invention as recited in the appended claims.

ILLUSTRATIVE EXAMPLES

[0025] Examples 1-4 illustrate various methods for manufacturing the particulate of this invention. Wax coated particulate was also prepared for comparison against those of the invention.

Example 1: Fluidized Mill

[0026] A porous silica particulate sold by Grace GmbH & Co. KG as SYLOBLOC® K500 anti-block and 15% by weight of various waxes were mixed in a fluidized mill to form coated anti-blocking agents. These mixtures were put through an Alpine™ fluidized mill at temperatures of 160 to 210° C in order to melt the wax on the silica surface, resulting in coated silica with a carbon content from 0.7 to 10%. These samples are those listed as A, B, and F-I in Example 5. SYLOBLOC K500 anti-block has an average particle size (APS) of 5 microns as measured by a Malvern Mastersizer particle size analyzer and a pore volume of 1.6 cc/g as measured by a Malvern ASAP nitrogen porosimeter. Pore volumes were measured after the sample was activated at 200° C for three hours. The vacuum applied was that programmed by the porosimeter manufacturer.

Example 2. Mixer

[0027] 250 g silica anti-block commercially available as SYLOBLOC® K300 and 25 g sorbitan monostearate were added in a 10 liter Henschel mixer. SYLOBLOC K300 has a pore volume of 1.6 cc/g, an average particle size of 3.6 microns and a surface area of 320 m^2/g. The mixer was externally heated to 60° C. The products were mixed with a rotation speed of 3800 rpm until a product end temperature of 60° C was reached. The end product had a carbon content of 6.3%.

Example 3. Fluid Energy Mill

[0028] A base silica gel with a pore volume of 1.6 ml/g, and a BET surface area of 260 m^2/g was used as starting material. This material was air milled to a particulate having an average pore size of 5.4 microns, using a 5 mm spacer mill and a throughput of 280 kg/h. This product was coated during milling by adding sorbitan monosterate in the jet to obtain 10% and 7.5% coating by dosing the sorbitate into the mill at rates of 28 kg/h and 25 kg/h respectively. This resulted in particulates having . carbon contents of 6.0% and 5.0% respectively.

Example 4. Fluidized Bed Dryer

[0029] 400 g of the SYLOBLOC® K500 anti-block mentioned in Example 1 and 60 g of Coatex DO-PP20 phosphoric acid ester were added into a 3 liter Heinen lab fluid bed dryer. The material was heated from 30° C up to 86° C by using heated air at a temperature of 100° C. The residence time in the fluidized bed dryer was 10 minutes at an airflow rate of 30 Nm^3/h. The air stream velocity was 0.28 m/sec. The end product had a carbon content of 9.3%.

Example 5. Dispersability

[0030] 5% silica masterbatches of the coated anti-blocks listed below were made in polypropylene (PP) on a Theysohn twin screw extruder. These masterbatches were then diluted with granulated PP while mixed in a tumbler mixer and then processed to produce films having a concentration of 2000 ppm (0.2%) silica on a Collin cast film line. The extruder conditions are indicated below.

Theysohn twin screw extruder 30/40D
Screen: 200 Mesh
Speed: 300 rpm
Temperature: 250-190°C
Products tested:

(1) Untreated SYLOBLOC® K500 anti-block
(2) Treated SYLOBLOC® K500 Anti-Block coated with A-J:

Trade Name	Product	Source	**Carbon** Content
A: OP	PP Wax	Hoescht	12.45%
B: PP 230	PP Wax	Hoescht	7.37%
C: Cithrol GMS	Glycerin Monostearate	Croda	12.2%
D: Crillet 4	Sorbitan Monooleate	Croda	9.4%
E: Crill 3	Sorbitan Monostearate	Croda	9.7%
F: Polywax 500	PP Wax	Petrolite	2.68%
G: Besquarc 195.	Polyethylene Wax	Petrolite	5.14%
H: Polywax 850.	PP Wax	Petrolile	4.55%
I: Polywax 1000.	PP Wax	Petrolite	2.68%
J: DO-PP20	Phosphoric acid ester	Coatex	9.5%

[0031] The cast polypropylene film were visually judged for nibs using the following ranking:

Disp. 1: well dispersed silica (relatively no nibs), e.g., < 500 nibs/m^2

Disp. 2: some minor silica nibs present ,e.g., < 1500 nibs/m^2
Disp. 3: a significant number of silica nibs present e.g., >1500 nibs/m^2, film quality not acceptable
Disp. 4: full of nibs, film unacceptable

[0032] Dispersability ranking of the films:

Sample	SL K500	A	B	C	D	E	F	G	H	I		J
Disp.	4	3	3	1	1	1	4	4	4	4		1

Example 6. Anti-blocking and Other Film Property Performance

[0033] Coefficient of friction, anti-blocking and optical (haze) properties were measured for SYLOBLOC® K500 anti-blocking agent (untreated) and SYLOBLOC® K500 treated with 7.5% by sorbitan monostearate (S.M.S.) and that treated with 10% sorbitan monostearate. The anti-block agents were added to a random polypropylene copolymer film at concentrations of 1000, 2000 and 3000 ppm. The treated anti-blocks were prepared using methods described earlier. 1000 ppm erucamide slip aid were also added to each sample. The films produced for these tests had a thickness of 35 microns.

[0034] The coefficient of friction values (measured one and seven days afterwards) are reported below.

Coefficient of Friction*			
Anti-block	Concentration	CoF after 1 Day	CoF after 7 Days
SL K500	1000	0.6	0.23
	2000	0.7	0.33
	3000	0.72	0.41
7%S.M.S.	1000	0.67	0.24
	2000	0.64	0.34
	3000	0.67	0.35
10% S.M.S.	1000	0.57	0.21
	2000	0.63	0.35
	3000	0.65	0.40

*Measured per ASTM D 1894-73 using a conventional friction/peel tester. The above values are averages from tests on three identical specimens (170 mm x65 mm) which are drawn at 15cm/mm for twenty seconds.

[0035] Blocking values for the above films are reported below.

Blocking Values*			
Anti-block Conc./ppm	1000	2000	3000
SL K500	0.38	0.19	0.17
7% S.M.S.	0.30	0.20	0.15
10% S.M.S.	0.37	0.17	0.14

* Force/100 = Newton Force (F) measured in grams of weight needed to separate two films made from test material. Force measured using DYNISCO "Kageness" electronic Block-Reblock device. Films were first pretreated by storing films at 23°C at 50% relative humidity for twenty- four hours (24h). The films were then deblocked and blocked at 70°C under a load of 0.8N for one hour and at 23°C for a second hour at the same load. Then blocking values were measured using ASTM D3354.

[0036] Haze was also measured for the above samples. Haze is an effect arising from large-angle scattering of light. Lower value numbers refer to clearer films. The values below were reported from a Hazegard Plus ™ device from Gardner, while using conventional conditions and standards (Haze Standard H 10, Cat. No. 4742, Serial No. 635709 and where the control had a value of 11.4). Haze is measured pursuant to ASTM D1003.

Haze Values*			
Anti-block Conc./ppm	1000	2000	3000
SL K500	1.8	3.3	5.1

(continued)

Haze Values*			
Anti-block Conc./ppm	1000	2000	3000
7% S.M.S.	1.7	3.4	4.9
10% S.M.S.	2.0	3.3	5.0

[0037] Dispersability of the above examples was also measured by a visual evaluation as well as by counting the nibs and by measuring the pressure build up at the end of the extruder.

Dispersability Silica Concentration 2000 ppm			
	Visual[1]	Nib/Counting[2]	Pressure Test[3]
SL K500	4	3000 Nibs/m^2	4.55 dp/dt
7% S.M.S.	2	707	0.33
10% S.M.S.	2	792	0.6

[1] Visual Judgment
The amount of nibs in a film is judged visually and ranked according to the following values:
1. hardly any nibs present
2. some nibs present
3. a lot of nibs present
4. full with nibs

[2] Nib Counting
1x5 film is moved on an overhead projector. The number of nibs of different sizes are counted on a calibrated wallchart. Nibs are counted with sizes in the range of 0.2 mm to 1.5 mm. The total number of nibs per square meter is then calculated.

[3] Pressure Built Up Test
A 4% silica containing masterbatch is fed into a single screw extruder which contains a screen package (20μ). The pressure before the screen is measured as a function of time. The result is then expressed as dp/dt (pressure increase over time). The lower dp/dt, the better the dispersability.

Example 7. Dispersability Comparisons

[0038] The dispersability of this invention (porous silica particulate coated with sorbitan monostearate) was compared to particulate added to polymer separately from the monostearate, as well as compared to a particulate prepared by simply mixing the two components before adding the components to a polymer.
(i) Samples

Sample 1: SYLOBLOC K500 anti-block coated with 10% sorbitan monostearate (product was coated during milling). The method described in Example 3 was used to coat this sample.

Sample 2: SYLOBLOC K500 anti-block mixed with 10% sorbitan monostearate in a tumble mixer at ambient temperature.

Sample 3: The sorbitan monostearate was added to polymer separately before adding SYLOBLOC K500 anti-block silica. The amount of stearate added was 10% by weight of silica. Polymer and stearate were first tumble mixed at room temperature and then fed into extruder. Silica was then added to the polymer downstream.

Sample 4: SYLOBLOC K500 anti-block alone.

(ii) **Preparation of Masterbatches**

[0039] Polymer masterbatches were made from the above samples on a Theysohn twin screw extruder (30D). 5% of the sample particulate was added to a polypropylene homopolymer resin (Eltex HV 001 PF-Solvay) using a side feeder into the polymer stream. For Sample 3, the sorbitan monostearate was mixed with the HV 001PF polymer resin, followed by downstream addition of SYLOBLOC K500 into the extruder. The extrusion conditions for all the samples were:

Extrusion temperatures	230°C
Throughput	12 kg/h
Screen package	200 Mesh

(iii) Preparation of films

[0040] The masterbatches from (ii) were diluted with a EP1X30F (Montell) polypropylene random copolymer with ethylene. Crodamide ER slip aid was also added via a 5% masterbatch to obtain an end concentration of 1000 ppm anti-block in the final film. Cast films were produced on a Dr. Collin™ cast film line under the following conditions.

Extrusion temperature	260 °C
Film Thickness	35µ

(iv) **Dispersability**

[0041] The number of nibs (undispersed silica) per square meter in the final film were counted.

Sample	Nibs/m^2
Blanc film (no silica)	365
Sample 1	1059
Sample 2	1467
Sample 3	3286
Sample 4	<10,000

[0042] The dispersability of the silica coated with sorbitan monostearate was unexpectedly better than silica added separately from the surface active agent. As shown above, the separate addition of sorbitan monostearate to the polymer had no pronounced effect on the dispersability since all films with more than 1500 nibs/m^2 are unacceptable in terms of film quality. Significantly improved dispersability is also seen over silicas which have simply been mixed with surface active agent prior to adding it to the polymer film.

Claims

1. A particulate comprising:

    (a) porous inorganic oxide; and
    (b) an ester-containing surface active agent wherein the average particle size of the particulate is in the range of 1 to 20 microns and the particulate has a carbon content in a range of 1 to 15% by weight of (a) + (b).

2. The particulate of claim 1 wherein (a) has a coating comprising (b).

3. The particulate of claim 1 or 2 wherein the particulate is prepared by co-milling (a) and (b) at a temperature in the range of 55 to 200°C.

4. The particulate of any of claims 1 to 3 wherein the particulate has an average particle size in the range of 1 to 12 microns.

5. The particulate of any of claims 1 to 4 wherein the particulate has an average particle size of 1 to 7 microns.

6. The particulate of any of claims 1 to 5 wherein (b) is a member of the group consisting of fatty acid monoglycerides, fatty acid sorbitan esters, fatty acid glycerin esters, fatty acid trimethylolpropane esters, fatty acid pentaerythritol esters, and mixtures thereof.

7. The particulate of any of claims 1 to 6 wherein (b) is a member of the group consisting of phosphoric acid ester, sorbitan fatty acid esters, and mixtures thereof.

8. The particulate of any of claims 1 to 7 wherein the particulate has a carbon content of 1 to 10% by weight of (a) + (b).

9. The particulate of any of claims 1 to 8 wherein the particulate has a pore volume in the range of 0.3 to 2.0 cc/g.

10. The particulate of any of claims 1 to 9 wherein the particulate has a pore volume in the range of 0.8 to 2.0 cc/g.

11. A polymer film comprising 0.001 to 2.0% by weight of the particulate according to any of claims 1 to 10.

12. The film of claim 11 wherein the polymer comprises polyolefin.

13. The film of any of claims 11 to 12 wherein the film has a thickness in the range of 0.5 to 100 microns.

14. A method of preparing a particulate anti-block agent comprising:

(1) combining porous inorganic oxide particulate with 1 to 15% by weight ester-containing surface active agent based on the weight of the particulate and agent;
(2) mixing the combination from (1) and recovering a particulate having an average particle size of 1 to 20 microns.

15. The method of claim 14 wherein the mixing is performed at a temperature of 25°C or more.

16. A method of imparting anti-blocking to a polymer film comprising:

(1) combining a polymer and a particulate according to any of claims 1 to 10; and
(2) forming a film from the mixture of (1) in a manner such that the film comprises 0.001% to 1% by weight particulate based on the total weight of the film.

17. Use of a particulate according to any of claims 1 to 10 as anti-blocking agent for polymer films.

18. Polymer masterbatch comprising polymer and 5 to 20% by weight of a particulate according to any of claims 1 to 10.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 11 0989

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 5 175 051 A (BOTHE LOTHAR ET AL) 29 December 1992 (1992-12-29) * column 2, line 7 - line 47; claims 1,3,7,11-13 * * column 4, line 36 - line 39 * * column 1, paragraph 1 * * column 4, line 45 - line 49 * * column 5, line 52 - line 55 * ---	1-8, 10-14, 16,17	C08K9/04 C08K9/00
Y	EP 0 496 150 A (KERR MC GEE CHEM CORP) 29 July 1992 (1992-07-29) * claims 1,3,6,8-10 * * page 2, paragraph 1 * * page 3, paragraph 2 * ---	1-18	
Y	GB 2 031 910 A (NL INDUSTRIES INC) 30 April 1980 (1980-04-30) * claims 1,4,6,8,9 * * page 2, line 36 - line 39 * * page 1, line 5,6 * ---	1-18	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	21 February 2001	Lauteschlaeger, S

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EUROPEAN SEARCH REPORT

Application Number
EP 00 11 0989

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